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Ordered and Ultra-High Aspect Ratio Nanocapillary Arrays as a Model System

Mitchell L. Solomon, Philip Cox, Nicholas R. Schwartz, Gregory E. Chester, and Justin J. Hill

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14. ABSTRACT

Nanocapillary arrays are attractive structures for many applications due to the relative ease and scalability of the self-assembly process of their formation. The high surface area-to-volume ratio of these structures can benefit a wide range of energy technologies such as photovoltaics, electrochemical capacitors and batteries, as well as a range of chemical technologies such as separations, storage and catalyst scaffolding. We are currently demonstrating their utility for high density storage of gases such as hydrogen and oxygen. Their high aspect ratio and ordered arrangement is advantageous for low-cost, bottom-up, templated nanostructure growth and ordered assembly at the device scale. Assembly of nanostructures the device scale in the absence of a templating structure, while maintaining the benefits of a nanomaterial, is often the dominant technical hurdle for implementation of nanomaterials into technologies. In previous work we have used AAO templating to maintain nanostructure benefits for photoelectrochemical cells with areas exceeding several square centimeters. Furthermore, the confined radial dimension of nanocapillaries can be used to synthesize molecularly confined or form quantum confined nanostructures. We have shown these effects benefit to improve double layer capacitance, as well as improving the figure of merit in nanostructured thermoelectrics. Specifically of interest in this discussion is the formation and deep pore growth of anodized aluminum oxide (AAO)-based nanocapillary arrays as the basis for high density, safe and high rate gas storage devices. The target is to grow these ordered nanocapillaries structures to centimeters in length while maintaining a uniform 100 nm nanocapillary diameter and an overall structure that is 100's cm^2 in area. In order to produce these materials quickly, a hard anodization approach is used. Probing the limits of the fabrication has highlighted a fascinating system of interdependent length scales, transport and thermal processes, and current-potential distributions. Potentiostatic and linear sweep potentiometry during deep nanocapillary growth will be presented. Electrochemical impedance spectroscopy (EIS) of the electrolyte and within oxide barrier layer will be discussed; particularly the constant phase element dispersion behavior during deep nanocapillary growth that exemplifies this as a model electrochemical system for porous electrodes. Particularly the EIS response of the system during nanopore growth and its implications of growth mechanism and modes of failure will be presented. A discussion of the implementation of the experimental design and other factors will be discussed elsewhere.

15. SUBJECT TERMS
Nanocapillaries, templates, hydrogen storage, oxygen storage, electrochemical self-assembly, electrochemical gas compression, nanotechnology, carbon nanotube, nanoparticle, membrane electrode assembly, anodized aluminum oxide, nanocapillary arrays

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228th ECS Meeting
Wednesday, October 14 2015

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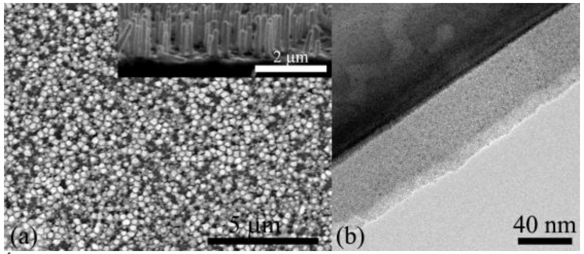
Agenda

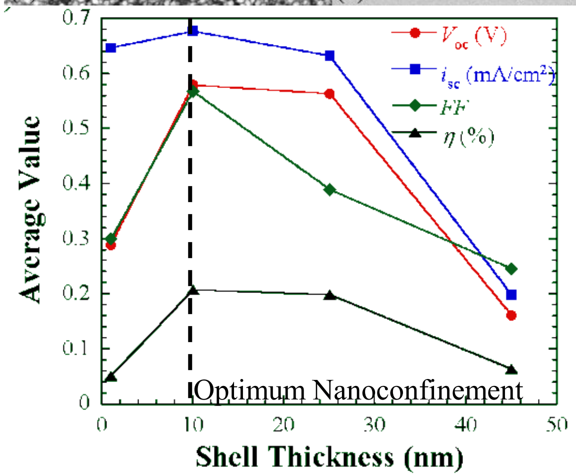
- AAO: Diverse Nano Applications
- Theoretical Considerations
- Characterizing Ultra-Deep AAO
- Future Work

Materials Science & Engineering – *Energy Conversion*

Solar Cells

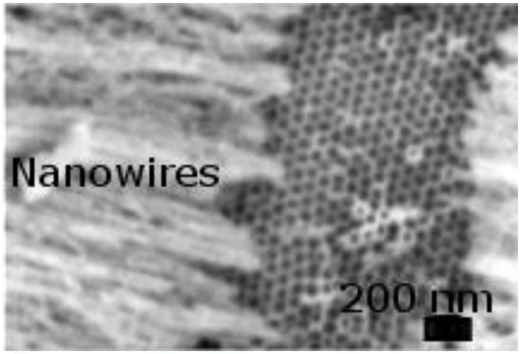
Photoelectrochemical Light/Electrical Conversion

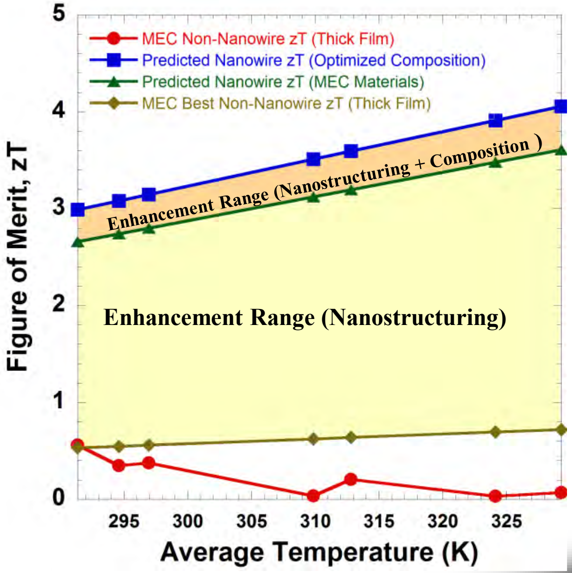




Thermoelectrics

Solid-State Heat/Electrical Conversion



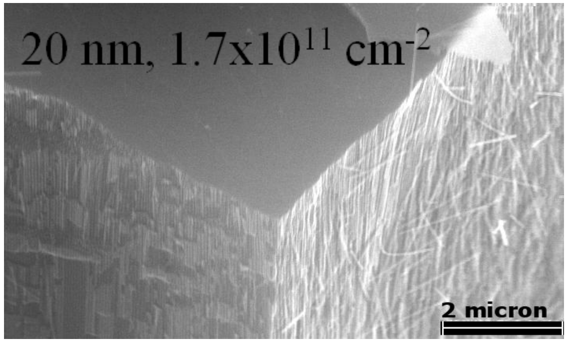


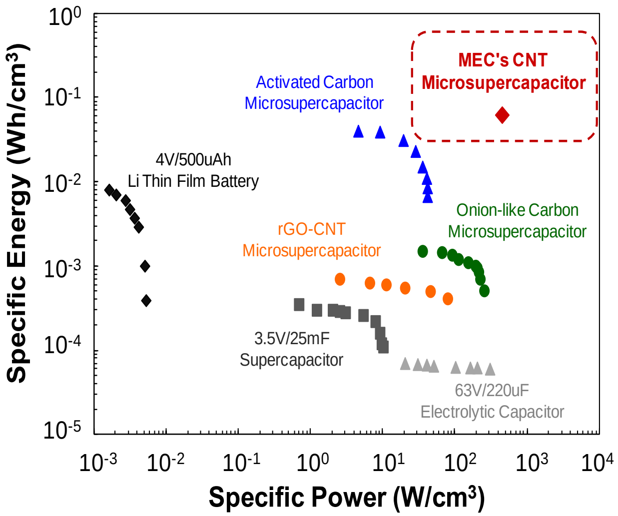
Mainstream leverages nanomaterials to enhance technologies based on bulk materials

Materials Science & Engineering – *Energy Storage*

Ultracapacitors

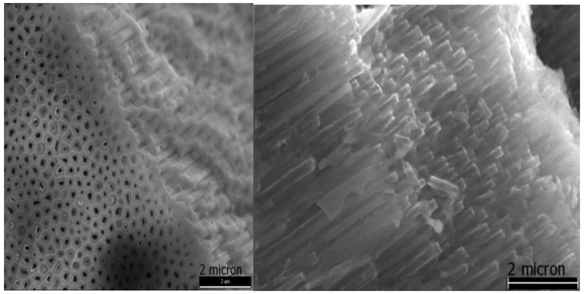
Electrochemical Energy Storage

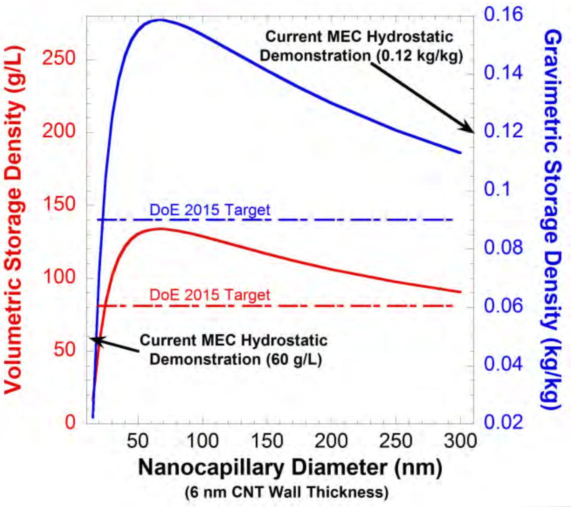


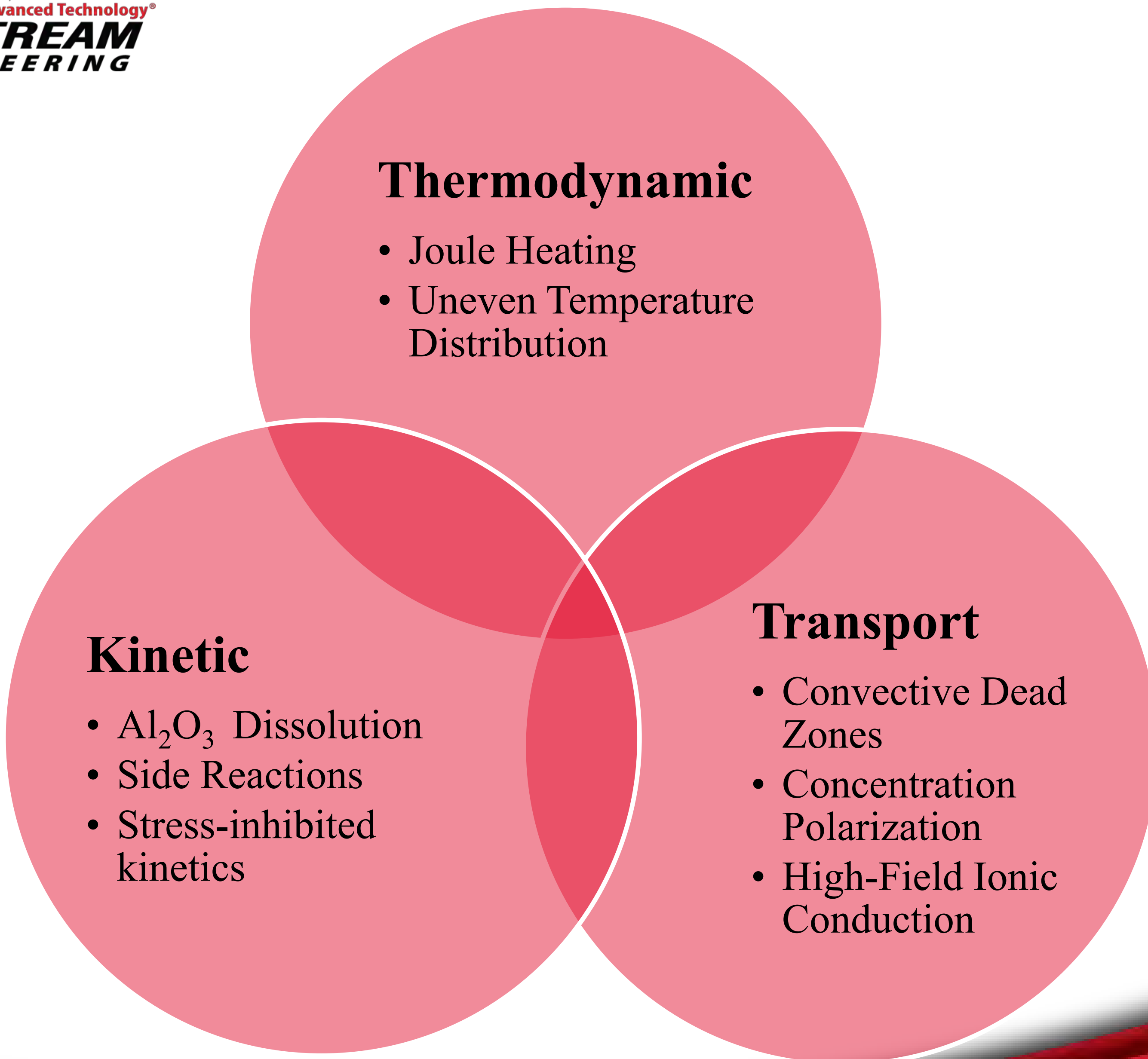


Nanocapillaries

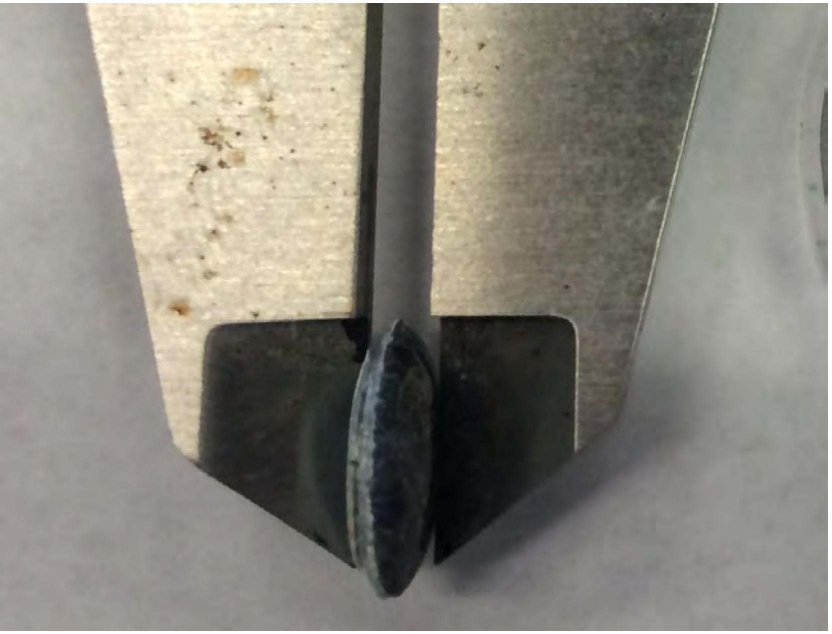
Hydrogen & Oxygen Storage





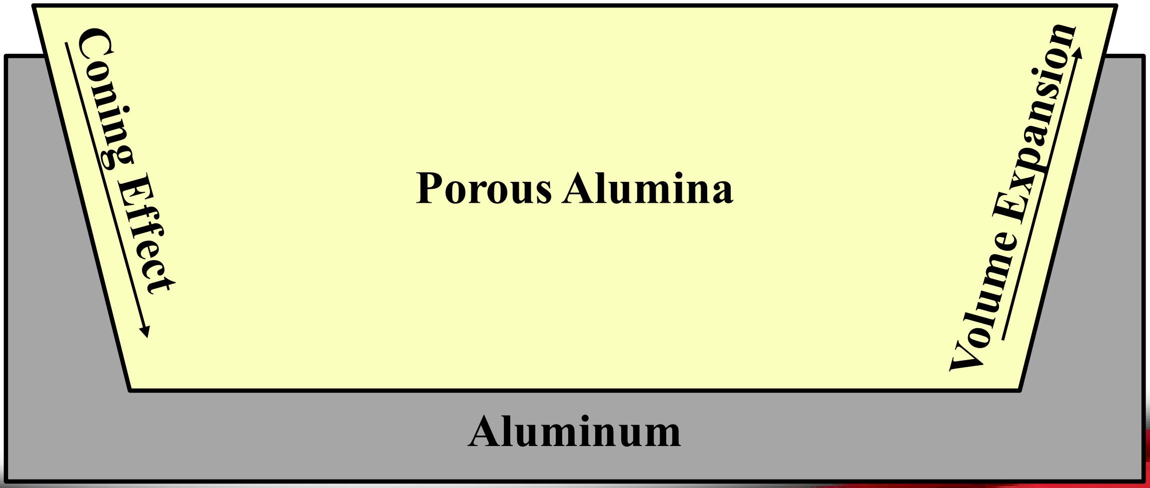

Thermodynamic
• Joule Heating
• Uneven Temperature Distribution
Kinetic
• Al_2O_3 Dissolution
• Side Reactions
• Stress-inhibited kinetics
Transport
• Convective Dead Zones
• Concentration Polarization
• High-Field Ionic Conduction

Issue: Conical Anodization



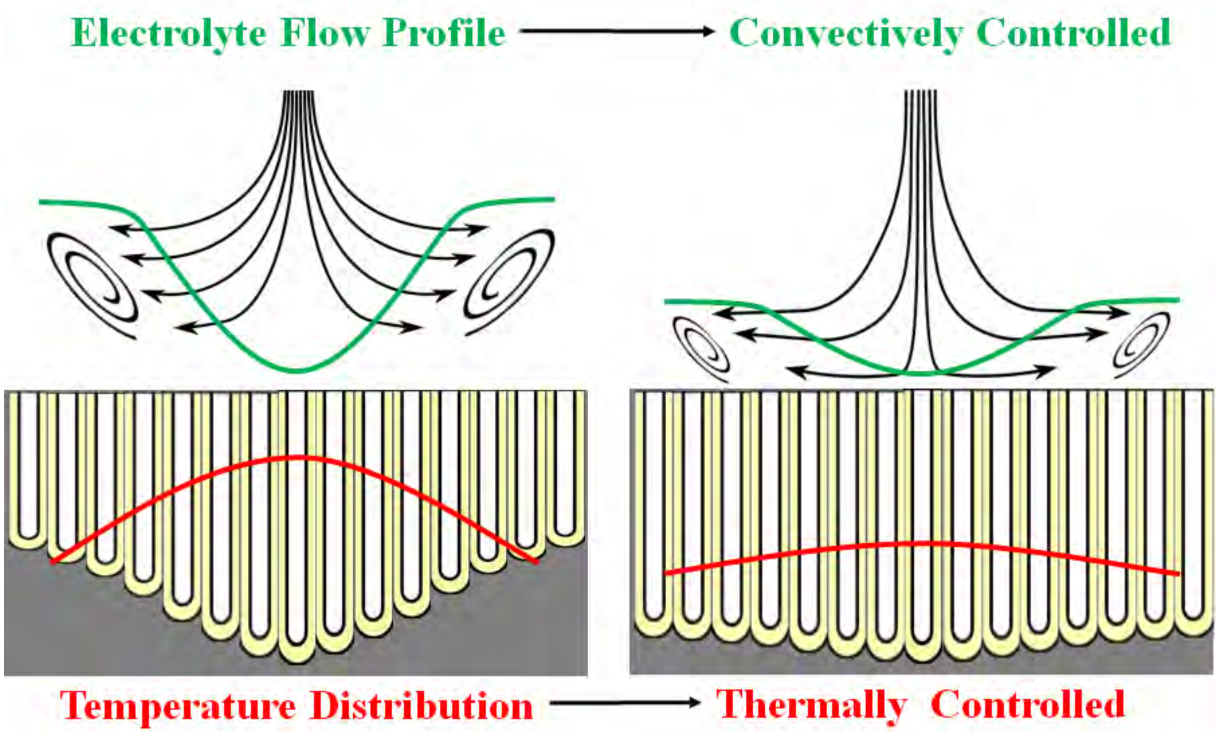
- Decrease storage volume
- Mechanical instability

- Causes:
- Leakage, stress-inhibited kinetics, uneven temperature distribution

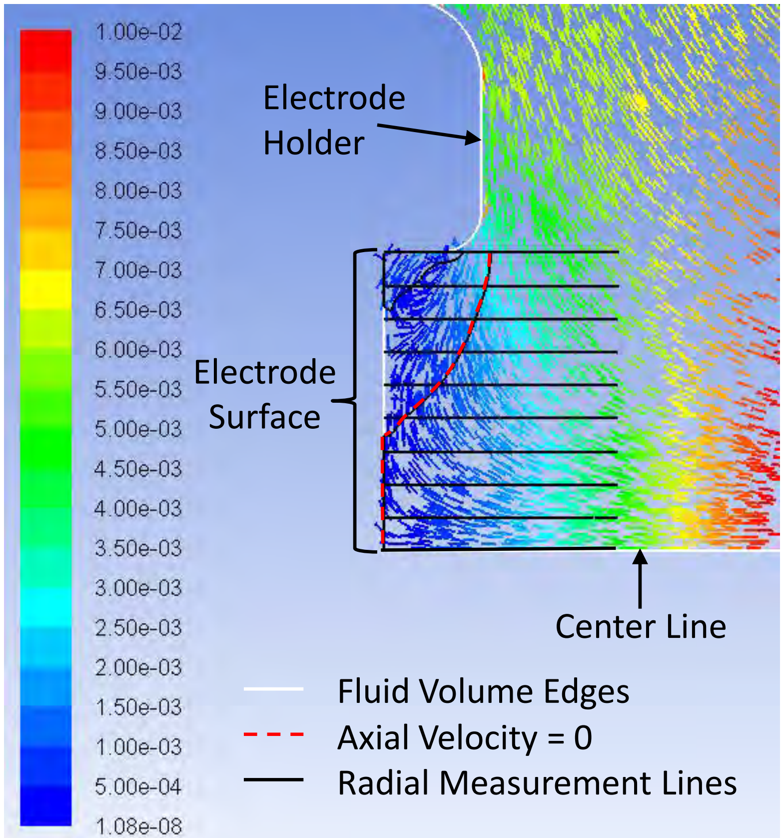


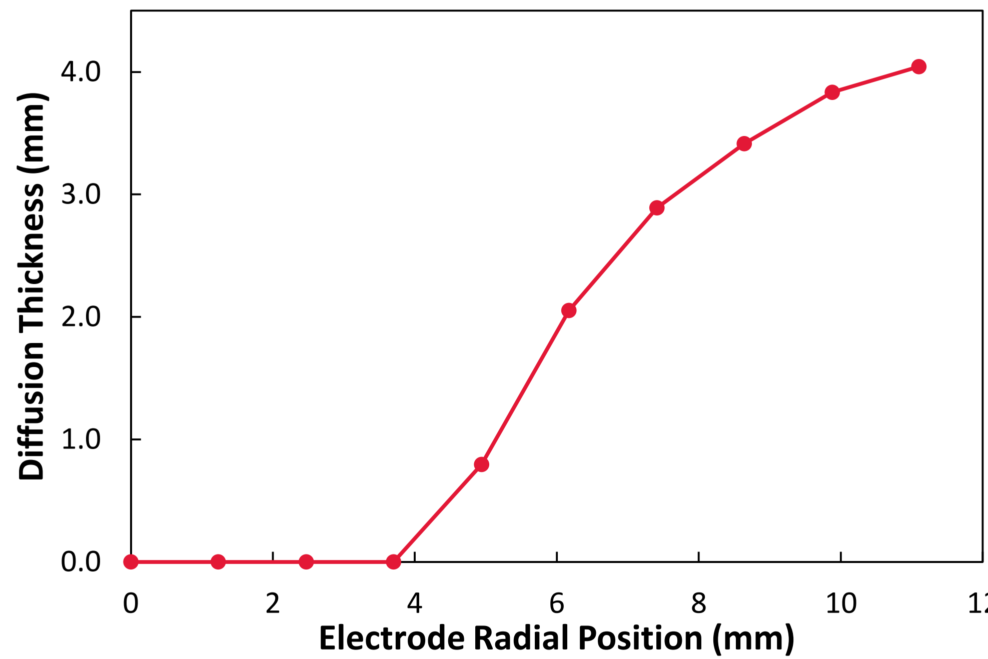
CPE Mitigation Schemes

- Control thermal and flow profile -> even anodization
- Maximize gas storage volume
- Rate of anodization benefits

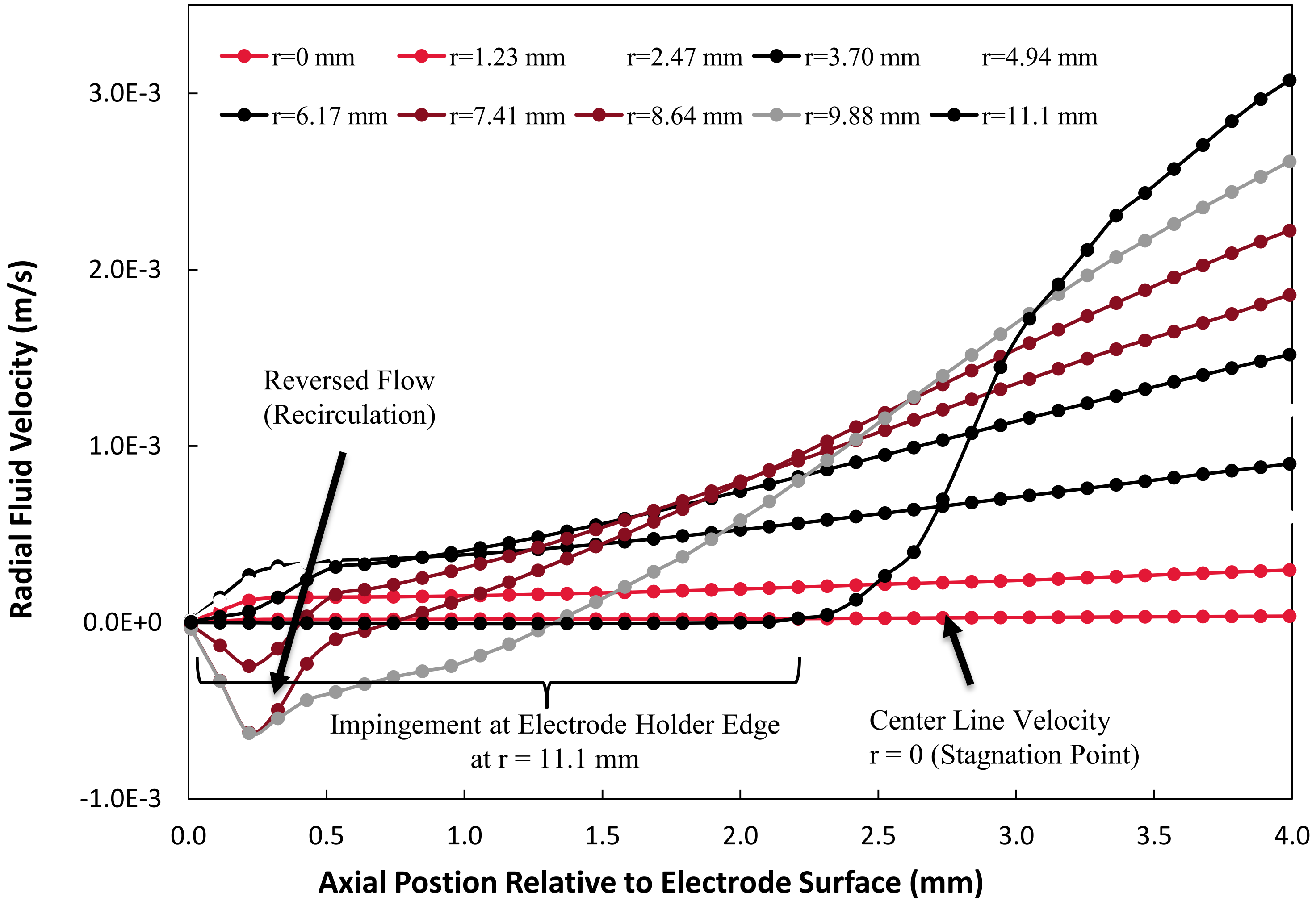


Fluid Flow and Diffusion Layer

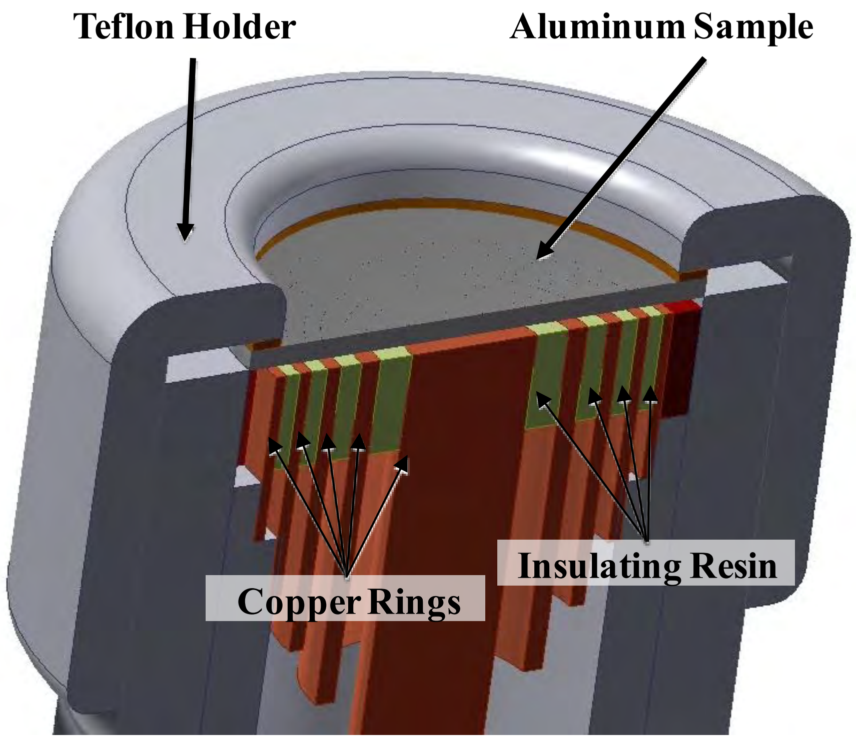


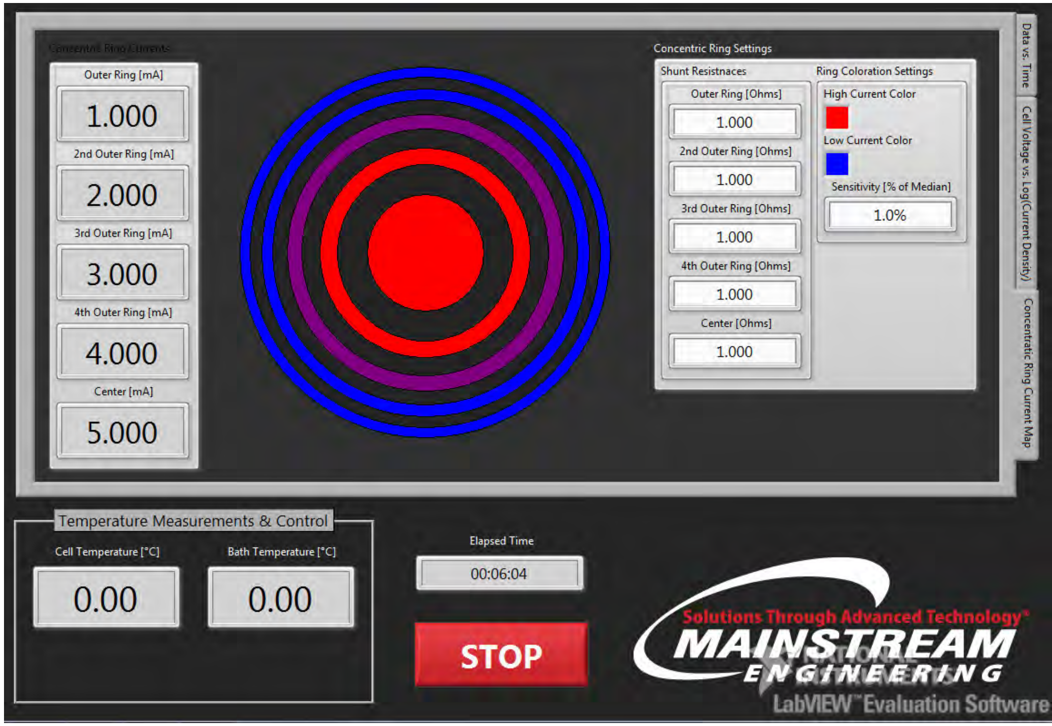


Fluid Flow Profile

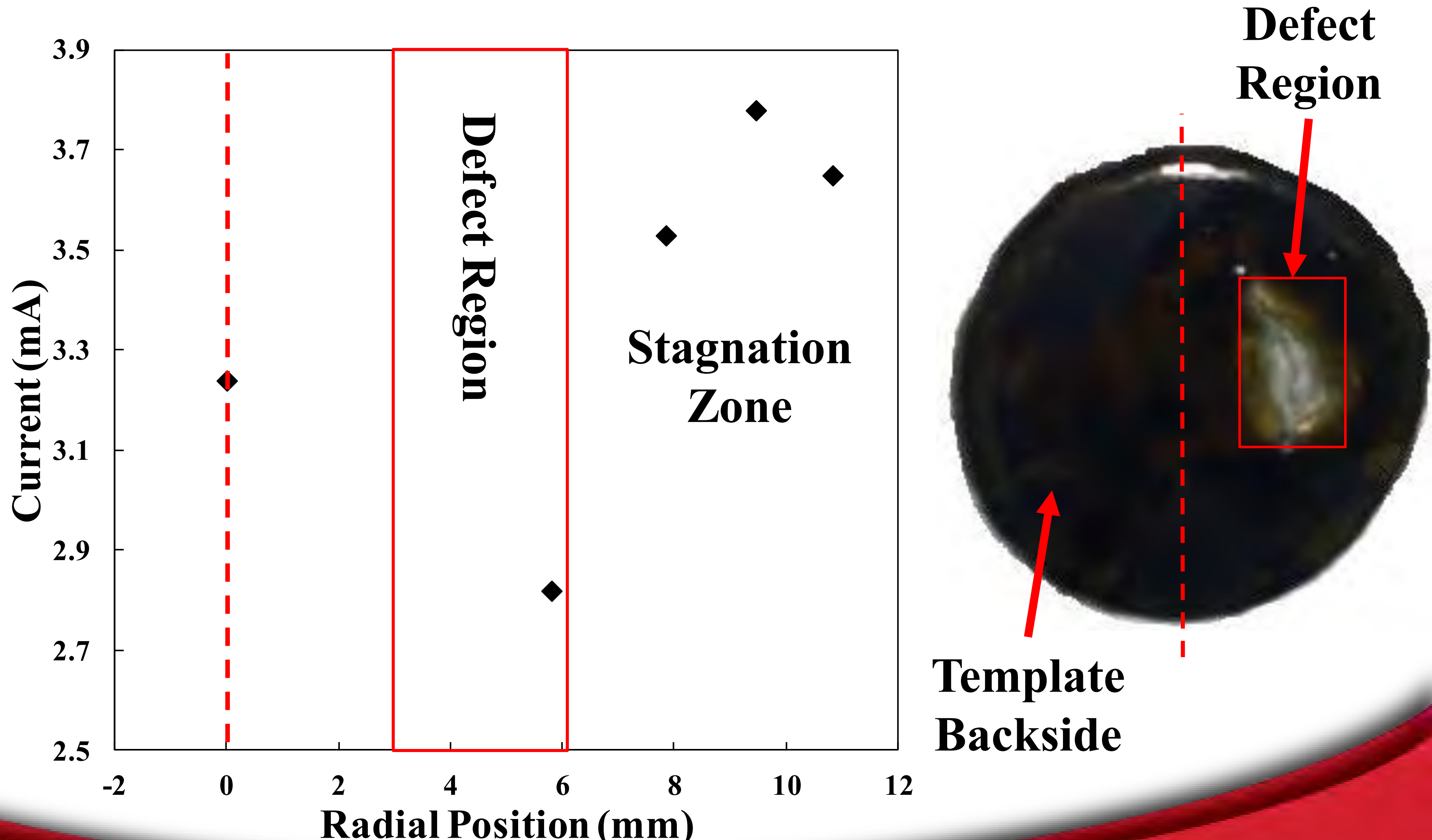


Current Mapping Hard Anodization



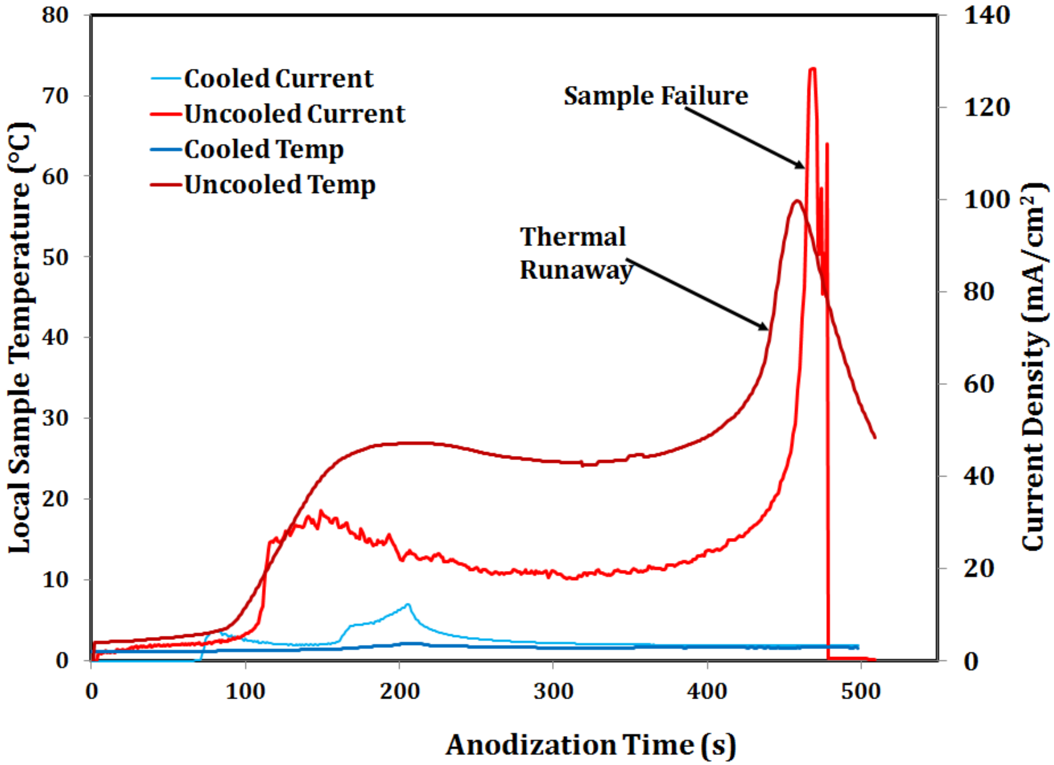


Defect Detection



Preventing Thermal Failure

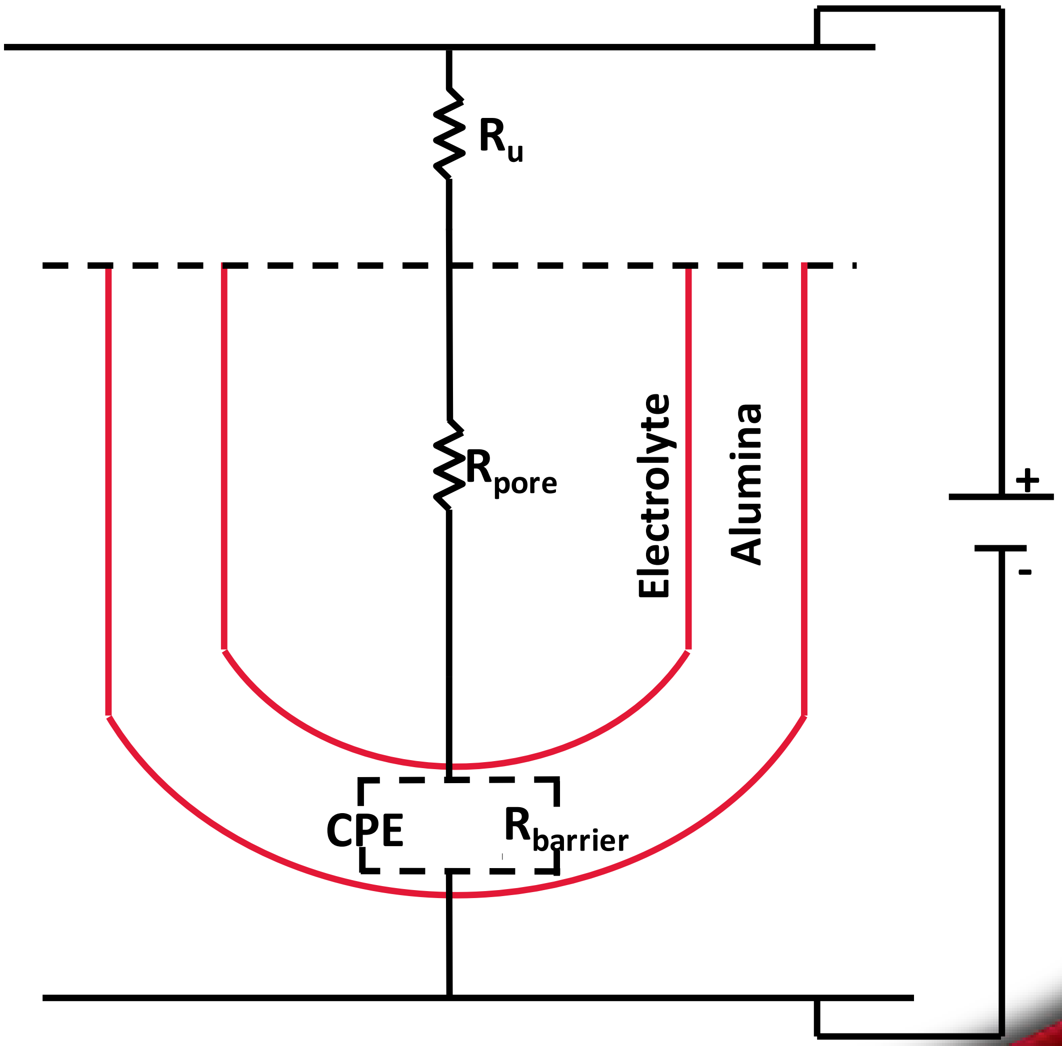
- Hard Anodization can reach up to 86°C locally!
- Initial thermal failure common and costly
- Two step anodization increases production complexity
- Answer: thermal control system



Template Equivalent Circuit

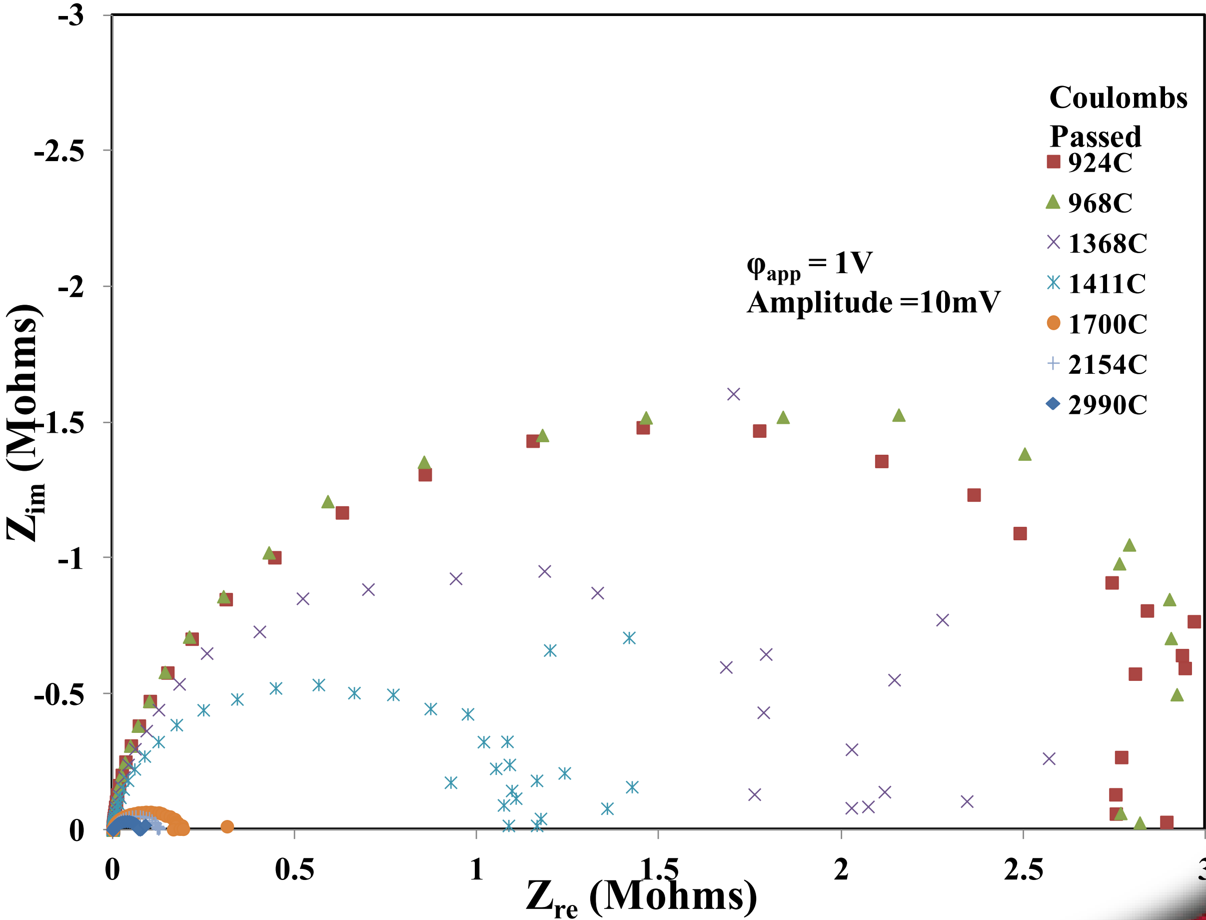
- **Bounded Warburg Diffusion**
- **Constant Phase Element**

- ***Indicates compositional dependence unevenly distributed***



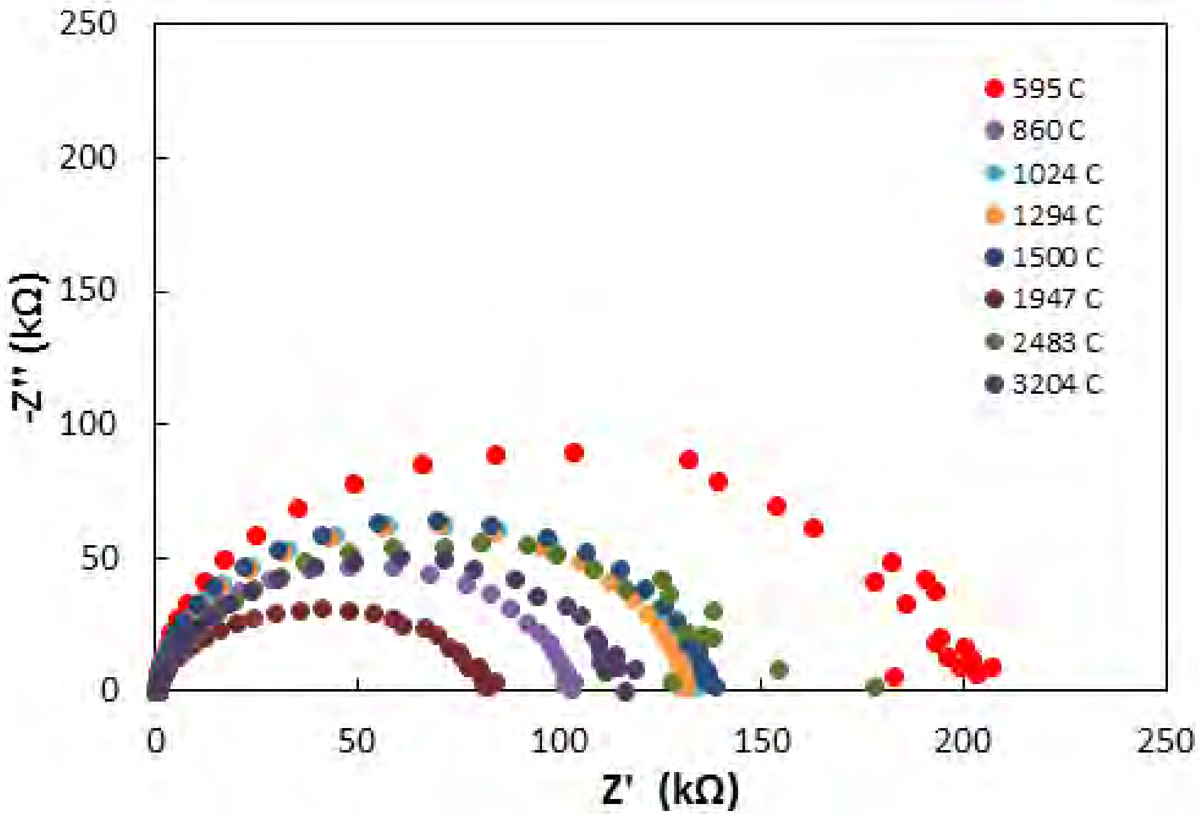
EIS Failure Mode Detection

- Large drop in charge transfer resistance
- Solution resistance increases ~depth
- CPE coefficient increased 3-fold
- *Indicates sample failure due to leaking*



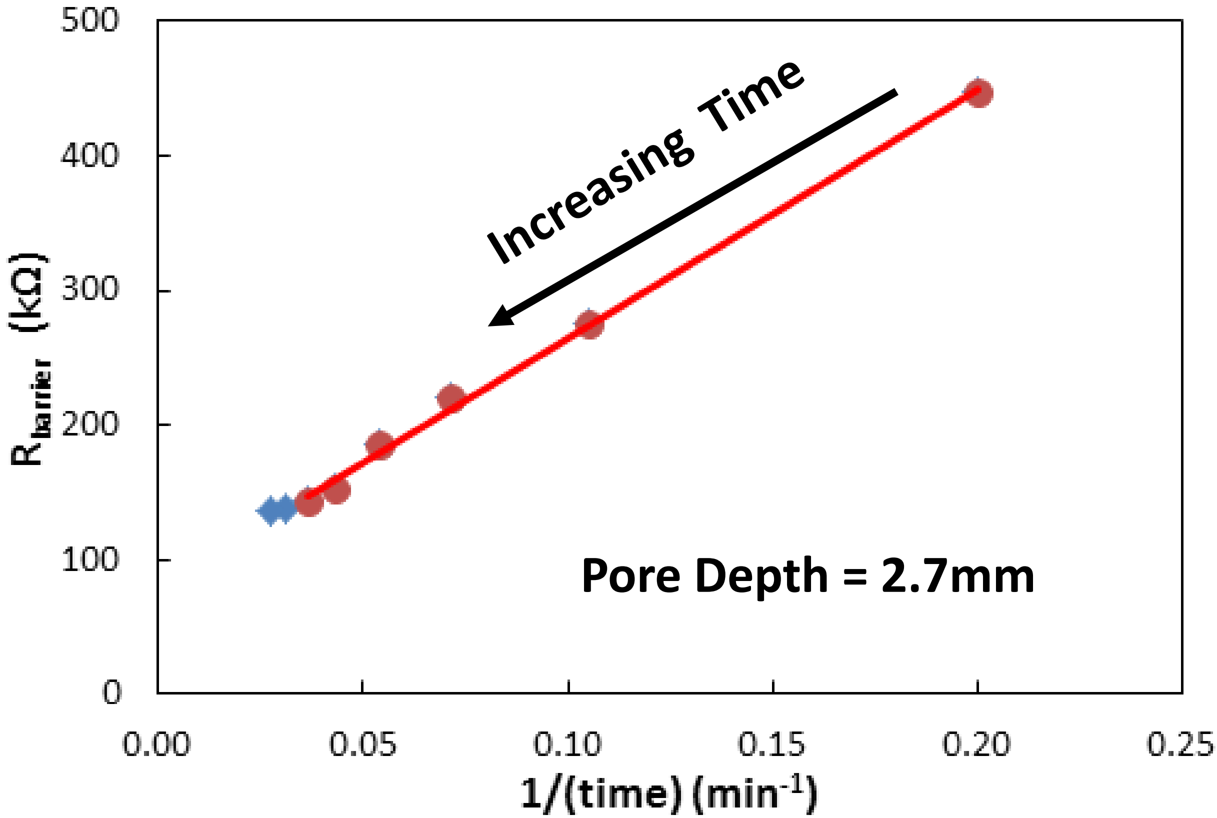
EIS Analysis of Deep Arrays

- **Charge transfer resistance varies due to impurities**
- **Solution resistance increases ~depth**
- **Weak increase in CPE Coefficient**



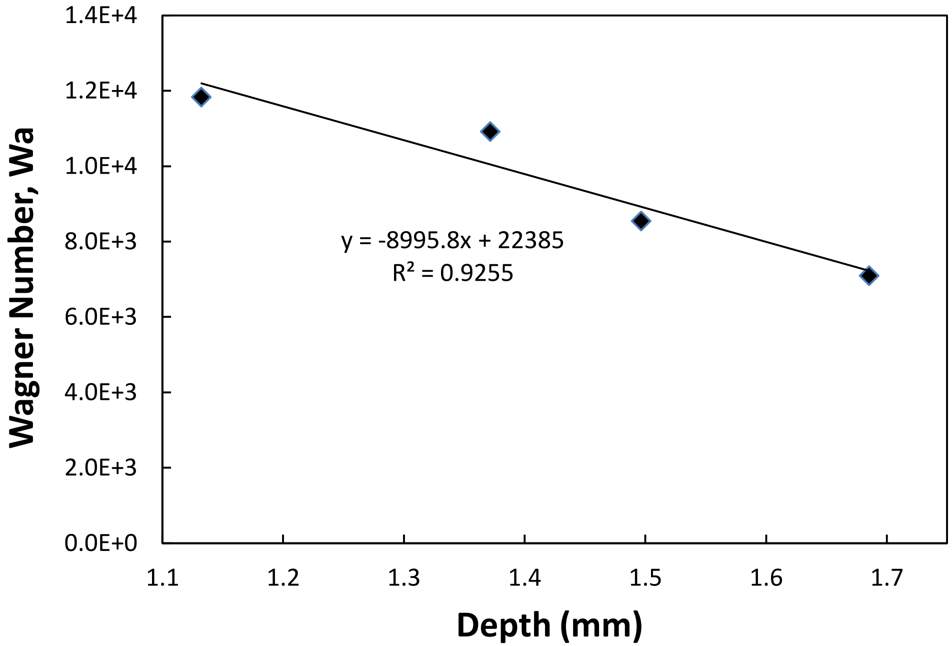
Barrier Layer Relaxation

- **30 minute relaxation time**
- **4-fold shift in low frequency impedance**
- ***Significant concentration gradient established during anodization***



Changes in Electrode Geometry

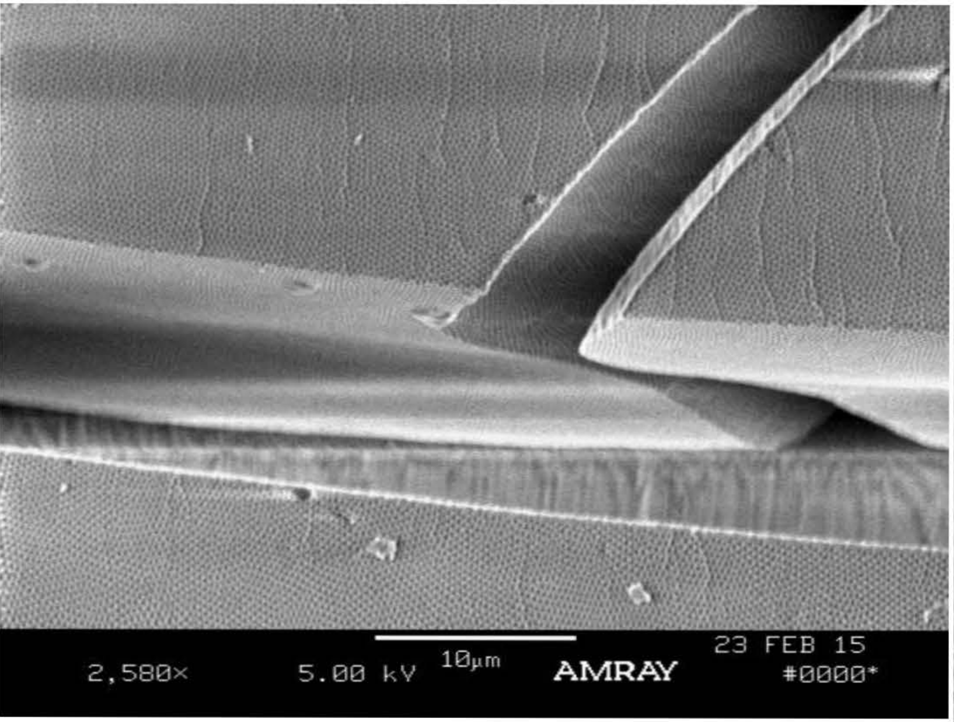
- W_a >> 10
- ***Significant change in electrode geometry vs depth***



Summary

- Technological progression → doorway to future innovations
- Creative test methods → model progression, failure identification
- Complex thermal/electrochemical dependence
  - Rate-inhibiting concentration gradient established
- Small environmental gradients effect long-term anodization
- Deep pore feasibility dependent on time/cost and anodization bath design

Questions?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5.00 kV
10µm
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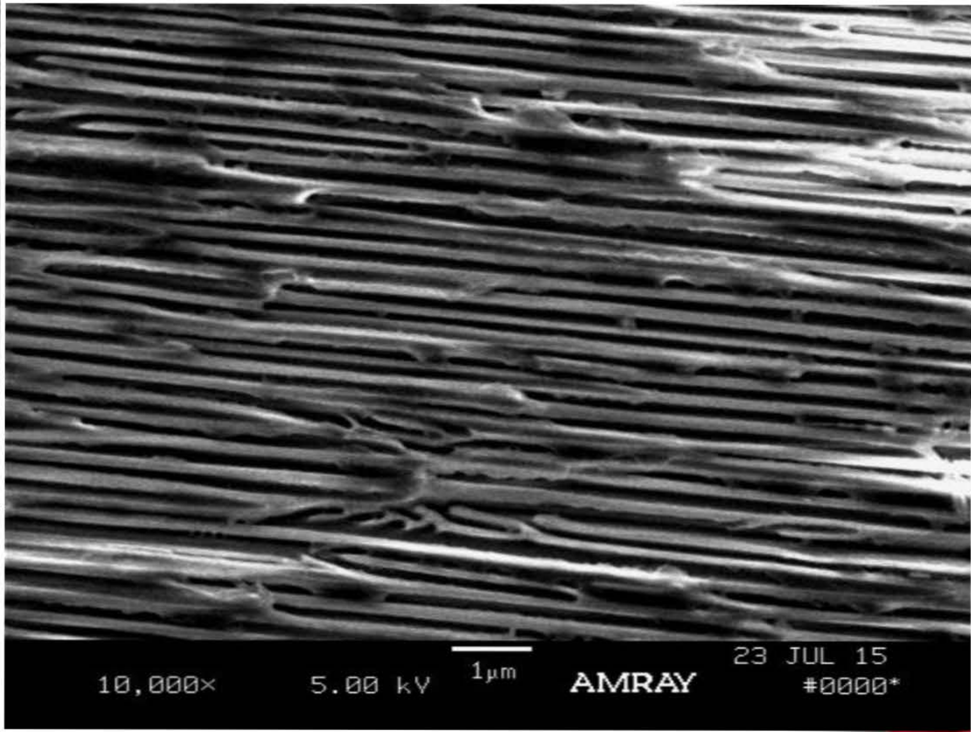
10,000×
5.00 kV
1µm
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